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SURVEY OF NICKEL-ALUMINIUM-BRONZE CASTING ALLOYS ON MAKINE APPL--ETC(U)
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REPORT

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**SURVEY OF NICKEL-ALUMINIUM-BRONZE CASTING ALLOYS
ON MARINE APPLICATIONS**

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G.M. Weston

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**DEPARTMENT OF DEFENCE
MATERIALS RESEARCH LABORATORIES**

REPORT

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**SURVEY OF NICKEL-ALUMINIUM-BRONZE CASTING ALLOYS
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G.M. Weston

ABSTRACT

The structure and corrosion performance of nickel-aluminium bronze (NAB), covered by naval specification DGS-8520 and DGS-348, have been investigated. No evidence was found to suggest that there would be any significant difference in corrosion performance between alloys meeting the two specifications. Early corrosion problems associated with the weld repair areas of castings have been overcome largely by using improved foundry and welding techniques followed by a heat-treatment procedure. Both crevice and pit corrosion still occur in operating systems. However, recent reports indicate that with improved NAB foundry practice this is less widespread, with penetration often being confined to the surface grains.

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ERRATA

Page 10. An additional last line should read "alluminium, nickel, and iron, with the last increasing with increasing"

Page 11, Line 1, should read "(Table VIII)"

Page 12, Delete Line 1.

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The structure and corrosion performance of nickel-aluminium bronze (NAB) covered by naval specification DGS-8520 and DGS-348 have been investigated. No evidence was found to suggest that there would be any significant difference in corrosion performance between alloys meeting the two specifications. Early corrosion problems associated with the weld repair areas of castings have been overcome largely by using improved foundry and welding techniques followed by a heat-treatment procedure. Both crevice and pit corrosion still occur in operating systems. However, recent reports indicate that with improved NAB foundry practice this is less widespread, with penetration often being confined to the surface grains.

TABLE OF CONTENTS

	<u>Page No.</u>
1. INTRODUCTION	1
2. BACKGROUND	1
3. ALLOY DEVELOPMENT	3
3.1 <i>Effect of Alloy Elements on Phase Boundaries</i>	3
3.2 <i>Influence of Individual Elements on Castability and Properties</i>	5
4. AS-CAST STRUCTURES	7
4.1 <i>Development of Structure</i>	7
4.2 <i>Phase Identification</i>	9
5. EFFECT OF HEAT-TREATMENT ON MICROSTRUCTURE AND PROPERTIES	10
5.1 <i>675° Heat-treatment</i>	10
5.2 <i>Effect of 800-830°C Heat-treatment on Microstructure</i>	11
5.3 <i>Examination of Some Locally-Available As-Cast and Heat-Treated NAB Alloys</i>	12
5.4 <i>Effect of Heat-Treatment on Mechanical Properties</i>	14
6. REPAIR OF CASTINGS	15
6.1 <i>Welding of Nickel-Aluminium Bronze</i>	15
6.2 <i>Effect of Heat-Treatment on Weld Deposit and HAZ</i>	15
7. TYPES OF CORROSION EXPERIENCED IN MARINE ENVIRONMENTS	16
8. CORROSION ASSOCIATED WITH WELD REPAIRED CASTINGS PRIOR TO HEAT-TREATMENT	17
8.1 <i>Corrosion Associated with Weld Repair</i>	17

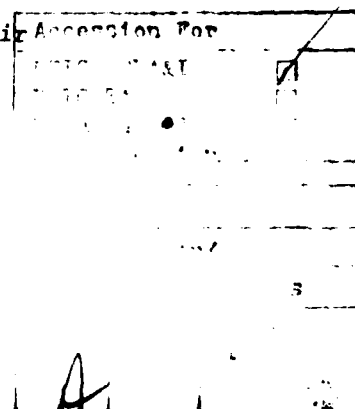


TABLE OF CONTENTS

	<u>Page No.</u>
8.2 General Corrosion on the Body of Castings	18
8.3 Corrosion Mechanism	18
9. EFFECT OF HEAT-TREATMENT ON CORROSION RESISTANCE	19
10. SUMMARY	20
11. REFERENCES	21

SURVEY OF NICKEL-ALUMINIUM-BRONZE
CASTING ALLOYS IN MARINE APPLICATIONS

1. INTRODUCTION

Nickel-Aluminium Bronze (NAB) casting alloys covered by the general specification BS 1400 AB2 are used extensively in naval applications. Within this general specification, the RAN has in present service valve, components from two different DGS specifications. Original castings were made to the UK specification DGS 8520 while recent castings have been made to its replacement DGS 348 [1,2]. Apart from small compositional variations, a major difference between these specifications is that the second requires a much lower heat-treatment temperature. Concern has been expressed [3], firstly, that the new specification may result in a lowering of corrosion resistance and, secondly, that there can be difficulty in obtaining specified elongation values in tensile tests. This report will therefore review the influence of alloy variations, micro-structural features, and heat-treatment temperatures on the mechanical properties and corrosion performance of NAB alloys within the above specification range. The effect of weld procedures on the corrosion resistance and mechanical properties is also discussed.

2. BACKGROUND

Fittings and valve components for both surface and submersible naval craft require a combination of properties including good resistance to sea water corrosion, and high strength coupled with adequate resistance to failure under shock loading. Valve components have in the past been made from gun metal but its strength is too low because of the greater operational depths required of modern submarines [3]. The NAB casting alloys covered by the general specification BS 1400 AB2, not only fulfil the above property requirements but also have a number of other useful properties not necessarily required in naval applications. These include good weldability, low coefficient of friction, low magnetic permeability, and resistance to softening at elevated temperatures [4]. Consequently these alloys are nowadays used extensively in marine applications.

General development of the NAB alloys at the British Non-Ferrous Metals Technology Centre, with the assistance of other research laboratories, resulted in the formulation of DGS specification 8520. This specification underwent minor modifications over the years resulting in DGS specifications 8520A to 8520F. However, these changes had little influence on the major problems associated with this alloy which had a similar compositional range to BS 1400 AB2, the composition ranges and minimum of mechanical property requirements for which appear in Tables I and II. Castings produced to this specification were introduced into Naval service for a wide range of applications. However, from the beginning, foundry casting problems were evident, arising mainly from the tenacious oxide-forming characteristics of the alloys and their narrow solidification range, which resulted in entrapped dross and shrinkage porosity and thus very high rejection rates. Of castings considered acceptable, nearly all had to undergo some form of weld repair ranging from superficial to full penetration welds. To alleviate problems of weld metal cracking a dual welding operation was used. Firstly an alloy wire "Nartrode S" having good high temperature ductility but low corrosion resistance was used to completely fill the weld cavity. The surface layer of this deposit was then ground back and replaced with an alloy "Nartrode E", known to have good sea water corrosion resistance.

In May 1974 during a submarine refit programme in the UK, valve castings were found to leak under moderate pressures [1]. Subsequent examination showed rupture through the casting wall (25 mm), in areas associated with previous weld repairs. Leaking was found to occur through a fissure in the centre of the weld deposit and was caused by removal of the protective "Nartrode E" deposit during finishing operations, thus exposing the low corrosion resistant weld deposit of "Nartrode S" to the marine environment.

More important, however, was the finding that heat-affected zone (HAZ) corrosion was widespread in most of the components examined. In some instances, cracking was associated with this corrosion. HAZ corrosion could extend as much as 20 mm from the fusion zone, and could be either continuous or intermittent around the weld periphery. At this time it was considered that the corrosion in the HAZ had occurred by selective attack of the κ phase, in contrast to corrosion in the weld material which occurred by the selective attack of the β phase. Cracking was found always to be contained within areas of the HAZ where a porous copper matrix had replaced the corroded alloy (dealuminization). Subsequent mechanical testing of material from these areas showed that the strength was markedly reduced but that the mode of failure under shock loading was still a ductile one.

Selective phase corrosion was identified at specific locations on castings which had not been repair welded, namely, areas such as flange faces where crevices were formed upon fit-up and beneath marine deposits on the surface. In some of the latter instances, the attack was confined precisely to the shape of the deposit. This form of corrosion could be quite insidious as it was difficult to detect because corroded alloy material was replaced by a similar volume of either porous copper or corrosion product. This form of corrosion generally was revealed only by a coppered appearance on the casting surface after cleaning.

As these problems immediately affected all submarines in service including those being refitted, a committee was formed to determine inspection procedures and to provide both short term solutions for recovery of partly corroded castings and long term improvements for new castings. No non-destructive method proved entirely successful in vetting a casting for continued service. However, data from the worst HAZ areas indicated that corrosion depth was a function of time and that the corrosion rate in these areas was of the order of 1 mm per year (up to 5 years). This enabled a value judgement to be made on the suitability of the castings for future service.

Concurrent work had indicated that selected phase corrosion could be related to microstructure with acceptable levels of corrosion resistance being provided by microstructures which did not contain any retained β phase or in which the κ phase did not form continuous networks at the α grain boundaries. The only practical alternative available was a heat-treatment which improved corrosion resistance while maintaining mechanical properties. The treatment selected consisted of heating to $815 \pm 15^\circ\text{C}$ for 1 hour per 25 mm of thickness plus 1 hour followed by cooling in still air. Such a thermal treatment reportedly optimised corrosion resistance with only a small loss in mechanical properties [2]. Slow cooling from this temperature restricted β formation, and prevented the formation of undesirable continuous networks of the κIII phase. This heat-treatment therefore was applied to all new as well as in-service castings. A single welding operation using corrosion resistant wire of base metal composition was also introduced.

Because of dissatisfaction with casting quality, a further committee was formed to improve the design and foundry technology of cast NAB. As a result of further experimental work and after liaison with the US Navy, a new specification DGS 348 (Tables 3 and 4) was introduced into service which included a heat-treatment of $675 \pm 15^\circ\text{C}$ for 6 hours followed by air cooling. This specification called for tighter control of the composition especially of the aluminium and of the overall purity level, virgin ingot material being specified. Limits are also imposed on the ratio of nickel/iron.

As the Royal Australian Navy has valve components from both specifications in service, concern was expressed that the lower heat-treatment temperature of 675°C might reduce corrosion resistance below that obtained with the earlier 800°C treatment.

3. ALLOY DEVELOPMENT

3.1 Effect of Alloy Elements on Phase Boundaries

It can be seen from the equilibrium binary copper-aluminium phase diagram (Fig. 1), that alloys containing up to 9.42% aluminium form a single solid solution (α) at room temperature. The strength and corrosion resistance of these alloys are found to be proportional to their aluminium content. Above 8-8.5% aluminium under casting conditions, or 9.4 wt% under equilibrium conditions, a β phase appears in the microstructure [4]. However, below 565°C

the β phase is unstable and, on slow cooling, is transformed to an $\alpha + \gamma_2$ eutectoid structure. This eutectoid structure confers higher strength than the single phase alloy, but at the same time it lowers the ductility of the alloy. Moreover, because the γ_2 phase (Cu_9Al_4) is richer in aluminium than either α or β it has a very much lower electrochemical potential and therefore has a propensity to corrode by galvanic action, and the corrosion resistance of the two phase alloy is lower than the single.

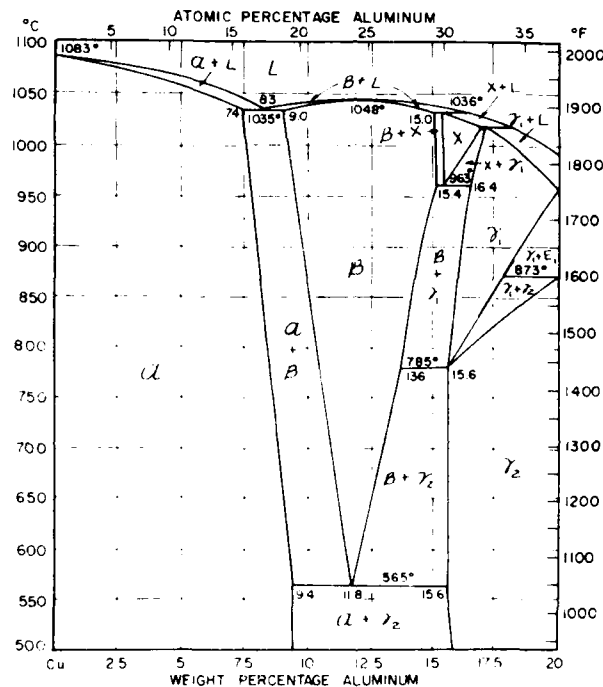


FIG. 1 - The binary copper-aluminum equilibrium phase diagram.

Quenching from above the $\gamma_2 + \beta$ region is one means of suppressing this reaction; however, there is always a danger that γ_2 will be formed either during quenching or subsequent weld repair operations [4]. This danger has been overcome by the addition of alloying elements which maintain the characteristically high strength, toughness, and corrosion resistance of NAB alloys without the formation of γ_2 . Both iron and nickel in amounts of up to 6 wt% have been added for this purpose. A comprehensive study of the structure and properties of the Cu-Al-Ni-Fe alloy system by Cook et al, [5]

has shown that the phases generally present at room temperature under equilibrium conditions are α , β , γ_2 and another phase, κ . (Fig. 2), already alluded to.

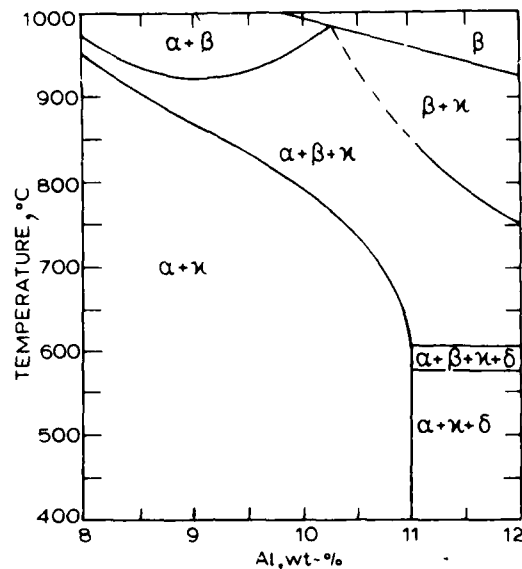


FIG. 2 - A vertical section of the Cu-Al-5Ni-5Fe equilibrium diagram showing the approximate relationship between composition, temperature and phase fields, after Cook et al [5].

Both iron and nickel combine with aluminium to form this new κ phase. Effectively this means that, by tying up aluminium in this way, the eutectoid phase boundary in Fig. 1 is moved to the right, and therefore larger amounts of aluminium (11 wt%) can be added under equilibrium conditions before the γ_2 phase is encountered.

Additions of manganese have been reported [6,24] to move the $\alpha/\alpha + \beta$ two-phase boundary towards the lower aluminium end of the phase diagram and therefore offset to a small extent the effect of both iron and nickel. It is reported that the addition of 1% Mn is equivalent to approximately 0.15% aluminium [24].

3.2 Influence of Individual Elements on Castability and Properties

Small variations in aluminium have been found to have a greater influence on mechanical properties than similar changes in either iron or nickel [1,6,13,14,18]. Increasing aluminium within the range 8.8-10 wt% has

been found to raise hardness, the proof stress from 200 MPa, to 277 MPa and the tensile strength from 600 MPa to 708 MPa [1]. This increase in strength is accompanied by a decrease in elongation values, attributed to the presence of κ III at the α grain boundaries [1,14,18,19]. To obtain the desired elongation values after heat-treatment in DGS specification 348, it has been reported that either alloy additions or aluminium values should be towards the lower end of the specification range [18]. Although an increase in the aluminium content improves corrosion resistance in the single α phase region, amounts approaching 10 wt% can give rise to a continuous grain boundary retained β phase in the as-cast structure and a lowering of corrosion resistance. Level of 9-10.5% aluminium has been reported to give the best range of properties for propeller manufacture, with alloys with 9.5% aluminium giving the best combination of properties including notch toughness, strength, ductility and weldability, when the nickel, iron and manganese were held at 5, 4 and 0.5%, respectively [20].

Iron within the range 0-5 wt% has been reported to have the largest effect in reducing grain size [16,20], and in restricting grain growth at elevated temperatures when present in amounts greater than 3 wt%, whilst also reducing the solidification range [16]. Increasing iron content within the range 3-5% was also found to increase proof and tensile strength, help retain strength at elevated temperatures, improve wear and abrasion resistance, and raise the fatigue endurance limit [16]. Iron in the range 3-5% appears to give the best combination of properties, with the optimum value probably closer to 4%.

Nickel within the range 0-5% increases proof and tensile strength, improves abrasion resistance, and has a grain refining effect somewhat less than that of iron [16]. It has been reported to retard the transformation of the β phase and to increase the hardness of both the hypoeutectoid and eutectoid aluminium-bronze alloys [22]. Alloys with nickel contents below 4%, with aluminium content in the range 9-11% and an iron content of 4%, are reported to be susceptible to severe second-phase attack in sea water with a concomitant loss in tensile strength [23]. In all these alloys, the relative amounts of iron and nickel are important. Values of iron greater than that of nickel can lead, on slow cooling, to the breakdown of the eutectoid structure and its replacement by a continuous or semi-continuous grain boundary network of degenerate κ III, depending on the composition and iron-nickel ratio. Structures with κ present in this form undergo a severe loss in strength, [19] and, because this degenerate κ phase is continuous at the grain boundaries, corrosion resistance is reduced. For maximum corrosion resistance the nickel content should be higher than that of iron [1,9], and this requirement has been included in the new DGS specification 348. Notwithstanding this, higher nickel values are known to promote the growth of lamellar κ III eutectoid which, if continuous at the α grain boundaries, may again lower both corrosion resistance and elongation values. Because of this, Zanis and Ferrara [24] have expressed some reservations on the need for this specification for a NAB with higher nickel contents. The optimum combination of properties appears to be obtained with nickel contents within the range 4-6%.

The presence of a small amount (<2 wt%) of manganese in NAB alloys improves the soundness of castings, probably by acting as both a deoxidant

[6,16,17] and as a scavenger for dross [13]. The influence of this amount of manganese on mechanical properties is uncertain [14], although larger amounts are known to improve strength and corrosion resistance [17]. Manganese has been reported to have a stabilizing effect on the β transformation [18,24]; consequently, the response of an alloy to heat-treatment is sensitive to manganese levels [1]. Manganese has also been reported to improve abrasion resistance and assist grain refinement [17]. Lowering the manganese levels to below 2 wt% is reported to reduce selective phase attack in sea water [1], due most likely to a reduction in the amount of the β phase retained in the as-cast microstructure.

4. AS-CAST STRUCTURES

4.1 Development of Structure

Several workers [5,7,8,9,10] investigating the relevant region of the 5% iron 5% nickel phase diagram (Fig. 2) have shown that these alloys solidify as a single β phase from which α and some κ precipitate on cooling to about 900°C. The α grows first at the β grain boundaries and along crystallographic planes to form a Widmanstätten structure [6,9,10]. A κ phase then forms which is iron rich and precipitates from the β phase in the form of coarse rounded or dendritic rosettes. Recent work suggests that this phase precipitates randomly in both the α and β phases [10]. At lower temperatures (<900°C) the remaining β is then transformed at temperatures around 850°C to a fine lamellar form of κ along with a rounded or cruciform form of κ in the α matrix. On further cooling to room temperature a fine spheroidal form of κ precipitates within the α grains. However, it has been reported [10] that, under cooling conditions of practical castings, all of these phase transformations take place at somewhat lower temperatures, as indicated in Table V. It has been shown that the lamellar κ phase can be continuous with the first precipitated rounded or rosette κ phase, indicating that the latter can act as a nucleant for the lamellar or rod like phase (Fig. 3).



FIG. 3 - Rosette κ I surrounded by lamellar κ III phase, after Culpan and Rose [10]. (x 6500)

Under equilibrium cooling conditions no β phase will be retained unless the aluminium content approaches 11 wt% (Fig. 2); however, under casting conditions some β is nearly always retained, and at higher aluminium content can form continuous networks at α grain boundaries [10]. Culpan and Rose [10] have summarized this transformation as shown in Fig. 4.

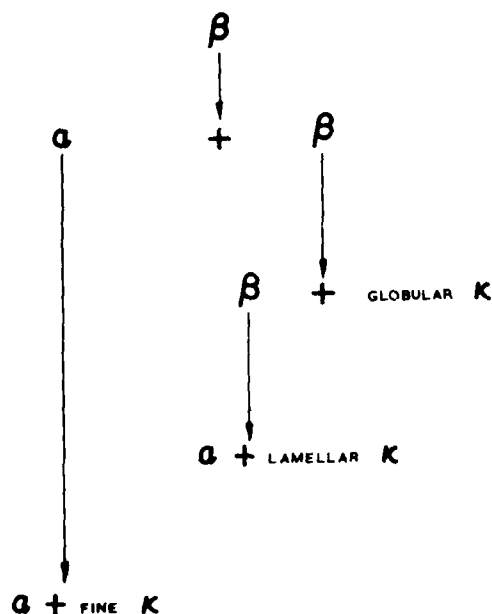


FIG. 4 - Schematic representation of the β phase breakdown after Culpan and Rose [10].

Work by Weill-Couly and Arnoud [11], using an electron probe microanalyser, identified the various forms of κ evident and have classified them as follows:-

κ I /a globular or rosette form of composition 69% iron, 13% copper, 13% nickel and 6% aluminium.

κ II /a small cruciform phase; composition not given.

κ III /a lamellar form of composition 26-43% iron, 13-20% copper, 23-34% nickel and 18-20% aluminium.

κ IV /a fine precipitate within the grains thought to be iron-rich.

A schematic representation of the κ phases prepared by these authors is shown in (Fig. 5).

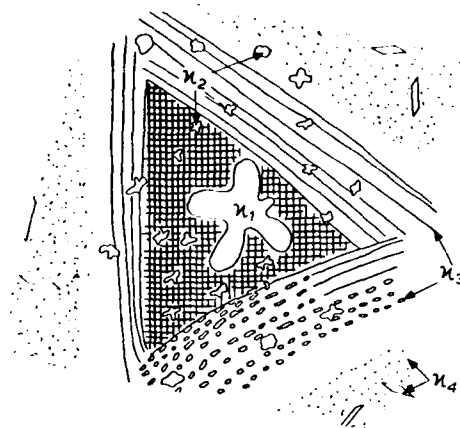


FIG. 5 - Schematic representation of κ -phases present in cast NAB after Weill-Couly and Arnaud [11].

In recent work Lloyd, Lorimer and Ridley [12] reported that the high temperature κ I phase was absent from their cast alloys, and suggested that it may be sensitive to cooling rate or slight variations in composition. These same authors, along with Culpan and Rose [10], have also identified two forms of κ IV within the as-cast α grains, spheroidal and cruciform, the latter being similar in morphology to the high temperature κ II particles. Both types of κ IV precipitate were found to be iron-rich, similar to the κ I and II phases. These phase changes have corresponded with alloy changes within the β phase on cooling from 900°C to room temperature. During precipitation of the κ I phase on cooling to 825°C, the iron content of the β phase decreases but the aluminium and nickel contents increase. At 820°C, precipitation of both κ II and κ III commences and there is a decrease in all three elements. The composition of α changed little over the temperature range, however the iron content decreased from approximately 5% at 900°C to 2.7% at room temperature [10]. This change is accounted for by the dense iron rich κ IV precipitation within the α grains at lower temperatures [4,10,11,12].

4.2 Phase Identification

Current work [10,12] has tended to concentrate on the morphology and chemical identification of the complex phases present, using the electron microscope supplemented by both wavelength spectrometer and energy dispersive analysis techniques. Results obtained by a number of workers are tabulated in Tables 6 and 7.

These results suggest that the various κ phases can vary in chemical composition from sample to sample and even within the same sample, indicating that they can exist over a wide range of composition [10,12]. Both the κ I, II and IV phases have similar compositions, rich in iron, and are thought to correspond to the $(\text{Fe, Ni, Mn, Cu})_3 (\text{Al, Si})$ complex based on Fe_3Al where nickel, manganese and copper may partially replace aluminium. It has been suggested [12] that κ IV may be a second-generation precipitate of κ II. Both have similar cruciform morphologies, but because of the very fine nature of κ II precipitates, analysis values hitherto reported may be unreliable. The same source reported the observation that κ II precipitated from an alloy with higher nickel and iron values and gave analysis values similar to those obtained for κ IV. There appears to be a significant compositional variation in the iron and nickel ratio for both the κ II and III phases, although both are precipitated from the melt at approximately the same temperature. In the case of κ II it is generally iron rich exceeding nickel by 5-10%, whereas in κ III nickel generally exceeds iron by a smaller amount [10]. Boundary surface analysis has indicated deposition of the lamellar κ III on the rosette κ I phase, and is consistent with the earlier observation (Fig. 3) of κ III growing from the surface of κ I rosettes [10].

5. EFFECT OF HEAT-TREATMENT ON MICROSTRUCTURE AND PROPERTIES

5.1 675°C Heat-treatment

A number of workers studying the heat-treatment of NAB alloys cast to compositions covered by specification DGS 8520E, [25] DGS 348 [26,27] and other similar specifications [4,10] have reported no change to the major as-cast phases on final cooling to room temperature. However, there has been general agreement that a 675°C heat-treatment would enable any β retained within the as-cast structure to be transformed to $(\alpha + \kappa)$ phases.

All of these workers reported the formation of a dense population of very fine κ particles within the α grains on cooling to room temperature. Detailed examination of these fine precipitates [10] showed them to be of two distinct forms. The first was spheroidal (approximately 1 μm in diameter) which on occasions resembled tiny κ I rosettes and was iron rich; this form was similar to that reported in the as-cast condition. The second was yet another distinct form designated κ V; these particles were cylindrical or lath-shaped (approximately 1 $\mu\text{m} \times 0.1 \mu\text{m}$) and were rich in both aluminium and nickel.

After increasing the heat-treatment temperature from 675°C to 840°C no spheroidal particles were observed, while the density of lath-shaped precipitates decreased and their particle size increased from approximately 1.0 $\mu\text{m} \times 0.1 \mu\text{m}$ to approximately 10 $\mu\text{m} \times 2 \mu\text{m}$ at the higher temperatures. A similar trend was also observed when the alloys were held for longer times (16 hours) at lower temperatures; this may possibly account for the improvement in ductility observed [25,27] after annealing at 675°C for long periods. As mentioned above, the new κ V phase was found to contain substantial amounts of

temperature (Table VII). This suggests that the iron atoms of the disappearing κ IV phase are taken up by the new κ V phase.

5.2 Effect of 800-830°C Heat-treatment on Microstructure

There appears to be some confusion as to whether the β phase is formed in lamellar κ III areas on holding in the above temperature range, subsequently transforming during air cooling. On the one hand, Culpan and Rose [10] claimed that heating an alloy of nominal composition 10% Al, 5% Ni, 5% Fe and 1% Mn up to 840°C and then air-cooling produced no change in the major as-cast microstructural phases, although it was acknowledged that heating within the temperature range 820-850°C could cause the alloy to enter the $\alpha + \beta + \kappa$ phase region depending on alloy variation within the specification. Upon entering this three-phase region and holding for an extended period spheroidization of the lamellar structure resulted as shown in Fig. 6. Even holding for times complying with DGS 8520E led to some breakdown of the lamellar phase [10]. The same authors [4] have recently reported no change in the major phases after heating a similar alloy up to 830°C which is the upper limit for DGS specification 8520E. Both reports [4,10] claimed that any β found during heat-treatment would be transformed to $\alpha + \kappa$ on cooling.

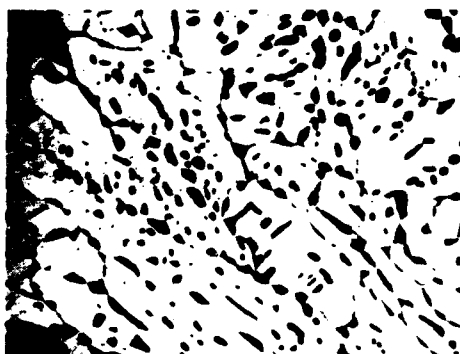


FIG. 6 - Breakdown of lamellar κ III after heat-treatment of 860°C for 72 h, after Culpan and Rose [10]. (x 480).

Other workers [29,34], however, have stated that κ III breakdown commences at 750°C and that this transformation to β can be completed at a temperature approaching 800°C. In one instance, [29] the Fe:Ni ratio was >1 and this encourages the breakdown of the lamellar phase. Other reports claim that the retention of β can be a problem on cooling from these high temperatures, which indicates some β formation (1,25,29).

temperatures, which indicates some β formation (1,25,29).

The κ precipitates within the α grains would be larger and more widely dispersed than those observed at lower temperatures and be of the κ V type (see Section 4.1).

5.3 Examination of Some Locally-Available As-Cast and Heat-Treated NAB Alloys

A microstructural examination was made of locally-available material to DGS specification 348* in the as-cast as well as in both the 675°C and 800°C heat-treated conditions. The samples provided did not indicate marked redistribution of

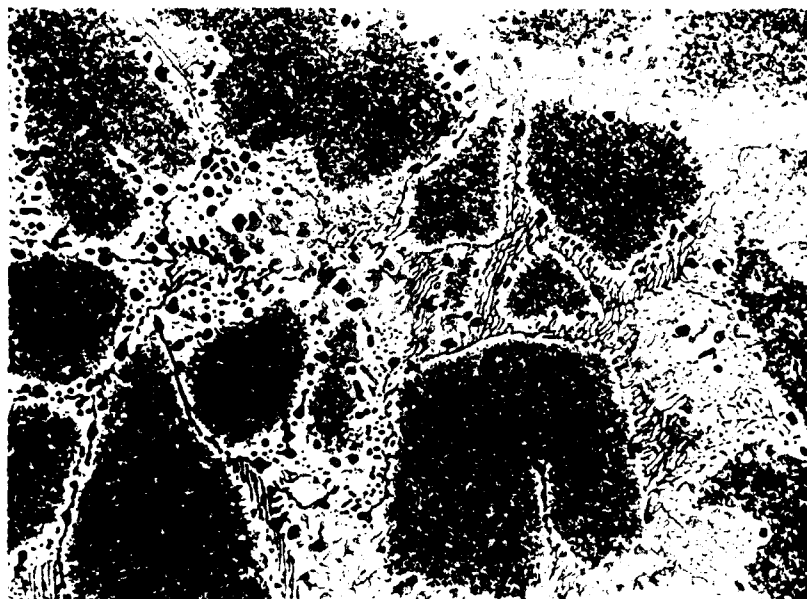


FIG. 7 - NAB DGS-348 after a standard 675°C heat-treatment showing the very fine κ V precipitation within the α grains (dark phase) surrounded by the $\alpha + \kappa$ III eutectoid. (x 500).

the major phases during heat treatment (Figs. 7 and 8). However, a small amount of retained β (1-2%) was evident in the high-temperature sample (Fig. 8). A piece of the as-cast material heated to 805°C and then quenched to room temperature contained 15-20% β in the lamellar region (Fig. 9). This amount

*Material was supplied by Garden Island Dockyard, Department of Defence.



FIG. 8 - NAB DGS-348 given a standard 800°C heat-treatment showing heavily precipitated α grains (light phase) surrounded by $\alpha + \kappa$ III eutectoid with some retained β (dark phase). (x 250).

of β would certainly vary with composition and heating temperature; consequently, heating at temperatures above 800°C could lead to retention of an unacceptable amount of β along with lamellar κ in very thin casting sections. Such a microstructure has to be avoided if maximum corrosion resistance is to be achieved, as mentioned earlier in Section 3 [1,25]. The wider range of manganese specified in DGS 8520E is undesirable in this respect, because higher levels would further assist the retention of β during cooling. Apart from the possible retention of β and some coarsening and spheroidization of the lamellar phase at the high temperatures, both heat-treatments still produced continuous lamellar κ and degenerated κ phases at the α grain boundaries.



FIG. 9 - NAB DGS-348 Quenched from 805°C showing retained β (dark phase) at the α grain boundaries. ($\times 250$).

5.4 Effect of Heat-Treatment on Mechanical Properties

In principle, the effect of lowering the heat-treatment temperature from 800°C to 675°C should be to raise the proof stress at the expense of elongation and notch impact toughness. It has been claimed [18,27,28] that, for an alloy cast to specification DGS 348, heating at the correct temperature of 675°C results in an increase in tensile strength and a decrease in elongation of approximately 5% from the as-cast values. Repeated heat-treatment cycles (up to a maximum of ten) produced no further lowering of ductility [26]. Morrison and Thorpe [27] found that this ductility loss could be recovered by heating at 710°C (Table IV), and recommended the use of higher heating temperatures as no major microstructural changes occurred which would affect corrosion resistance. Increasing the cooling rates has not been found to influence as-cast mechanical properties to any marked degree [19]. However, very slow cooling ($<0.8^\circ\text{C}/\text{min}$) between 810-600°C was shown to break down the lamellar structure resulting in a significant loss in proof stress [29].

6. REPAIR OF CASTINGS

6.1 Welding of Nickel-Aluminium Bronze

Initially, welding problems were experienced when using NAB wires of matching composition. Sub-surface cracking was found within the weld deposit, and was associated with the low strength and very low ductility of this material at elevated temperatures: a minimum in strength can occur at temperatures as low as 350-500°C [32]. As mentioned previously, this problem was initially overcome by using the inert gas MIG process with twin filler wires. A full penetration weld was first carried out with a copper-aluminium-iron alloy, commercially known as 'Nartrode S', which had good high temperature ductility but which produced a microstructure containing retained β phase around the α grains, resulting in increased susceptibility to sea water corrosion [1,4]. The surface layer of the deposit was then ground back and covered with a matching-base-metal weld deposit ('Nartrode E') known to have good corrosion resistance. As a result of damage or removal of the latter protective layer during finishing operations, problems with selective corrosion of the β phase were experienced during service. It was shown [32] that sub-solidus cracks in matching NAB welds could be avoided with careful inert gas weld procedures and control over tramp elements such as lead, tin and bismuth which are known to have a detrimental effect on hot ductility [4]. In fact, the newer DGS specification 348 calls for tighter control over tramp elements, which should reduce the degree of contamination of the weld metal.

Nowadays, all weld repairs are carried out using matching nickel-aluminium welding wire of type Bostrand AT-246 or Nartrode E [31]. The matching of weld metal composition is important as it has been shown that severe corrosion will result where there are significant differences in composition [33]. Because of the very fast cooling rates in welds the microstructure of the deposited metal consists of fine Widmanstätten α in a matrix of the retained high temperature β phase [4].

In the heat-affected zone immediately adjacent to the weld fusion boundary, areas of eutectoid $\alpha + \kappa$ revert to β , which is retained as martensitic β on cooling. The α phase remains essentially unchanged.

6.2 Effect of Heat-Treatment on Weld Deposit and HAZ

The effect of heat-treatment on both the HAZ and the weld deposit is similar. At temperatures above 600°C, retained β is transformed to a very fine dispersion of $\alpha + \kappa$ together with a fine dispersion of κV within the α grains of the HAZ [4]. Increasing the temperature of heat-treatment to 830°C coarsened the globular κ within the weld metal and on cooling to room temperature some β was retained at the grain boundaries of the parent metal structure.

7. TYPES OF CORROSION EXPERIENCED IN MARINE ENVIRONMENTS

There are a number of types of corrosion associated with NAB alloys in marine environments namely:

- (i) Pitting. This form of corrosion develops in localized areas in the component surface that is not attacked elsewhere to any large extent.

Continuously moving components are less susceptible to this form of corrosion.

- (ii) Crevice Corrosion. This form of corrosion occurs within or adjacent to a crevice formed by contact with a close-fitting object either metallic or non-metallic, such as marine growth on the surface of castings. A particular phase is corroded selectively. The lower oxygen potentials within the restricted areas can cause rapid corrosion of the more electronegative phases around the α grains, allowing them to be detached bodily [34].

- (iii) Dealuminization. This form of corrosion is particularly insidious and has been a major problem in submarine valve systems. Corrosion proceeds by the more electronegative phase dissolving and re-distributing copper in its place. The duplex $\alpha + \beta$ structures are claimed to encourage copper precipitation and the cementing of α grains in position [33,34]. This form of corrosion is difficult to detect because, although the re-distributed copper is porous and of much lower strength, it occupies the same volume and shape as the original constituent.

- (iv) Corrosion by Impingement. This form of corrosion is associated with turbulent flow. It is commonly found at inlet ends of condenser tubes. Corrosion of this type would have some erosive component and is causing some concern in Australian submarine systems [39].

- (v) Corrosion by Galvanic Action. This can occur where different alloys are joined in service. This form of corrosion has not been identified as a problem in operational systems.

8. CORROSION ASSOCIATED WITH WELD-REPAIRED CASTINGS PRIOR TO HEAT-TREATMENT

Selective phase corrosion of types (ii) and (iii) above have been the major concern in operational systems of modern submarines. These are the types commonly found in areas of weld repair and areas where crevice formation restricts oxygen access.

8.1 Corrosion Associated with Weld Repair

Severe corrosion in the HAZ has been observed to initiate in a zone 1-3 mm from the fusion line in some instances and propagate as a wedge into the parent metal (Fig. 10) [33]. More frequently, it has been observed to propagate as a very narrow band 1-2 mm wide in the parent metal running adjacent to the HAZ boundary where it may be of a continuous or semi-continuous nature (Fig. 11) [1,4,33,34].

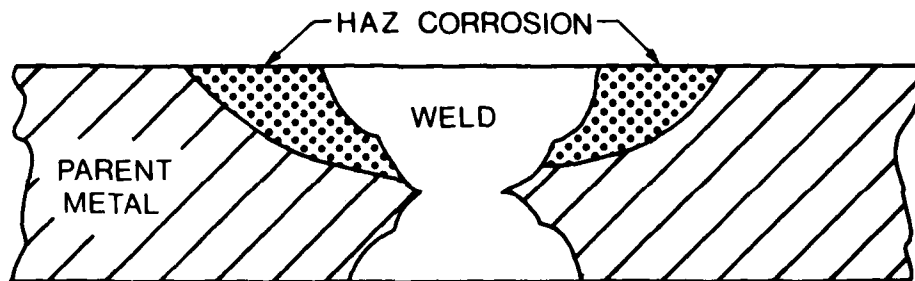


FIG. 10 - HAZ Corrosion propagating as a wedge into parent plate.

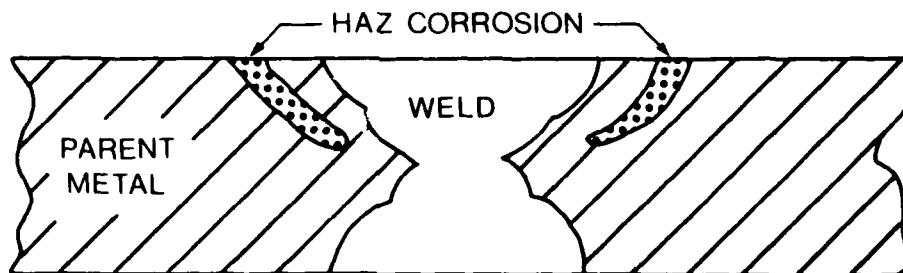


FIG. 11 - HAZ Corrosion propagating as a narrow band 1-2 mm wide running adjacent to the HAZ boundary.

Rapid selective corrosion of the β phase, followed in most instances by copper deposition, has been found to occur within the weld metal when matching weld deposits were not used [1,29].

8.2 General Corrosion on the Body of Castings

Plug or crevice corrosion on the general body of the castings was mainly associated with the formation of crevices at such places as tight fitting flanges or where debris build up and marine biofouling occurred, restricting oxygen access. (Fig. 12) [1,4,33,34].

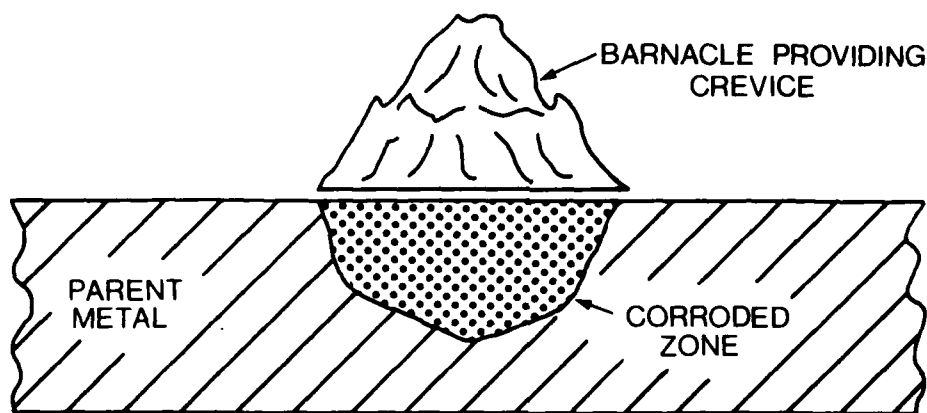


FIG. 12 - Plug of crevice type corrosion where marine biofouling has occurred.

8.3 Corrosion Mechanism

Early studies and reports [1,2,34,36] involving the mechanism of general HAZ corrosion considered that it was the κ III phase which corroded first around the α grains. However, other reports [33,35] claimed that κ III would only corrode in preference to α under crevice conditions, because under these circumstances insufficient oxygen would be available to passivate the κ III phase.

More recently, Culpan and Rose [4] obtained conflicting evidence from studies using the scanning electron microscope. They reported that the corrosion mechanism in the region of the HAZ/parent-metal interface prior to heat-treatment was by selective phase attack of the α phase followed by subsequent removal of the κ III phase.

Examination by scanning electron microscopy at MRL of corroded areas of as-cast DGS-348 has supported the viewpoint that it is the κ III phase which

corrodes first. Only a thin layer of biofouling was present on the surface of these samples.

This conflict of evidence may be resolved on the grounds of information [8,34] that the κ III phase may have a wide range of compositions which could make it either anodic or cathodic with respect to the α phase. It has also been claimed [34] that a small amount of copper in solution with the intermetallic κ III phase or a change in the corrosion environment can have a marked activating effect on this phase. Alloy variations, therefore, may account for the differences in observed corrosion behaviour.

Very fine $\alpha + \beta$ structures within the weld deposit and large κ I particles have been observed to remain unattacked under conditions where HAZ corrosion has occurred [4]. In the duplex $\alpha + \beta$ structure, where a porous copper sponge replaces the corroding β phase at the α grain boundaries, a much weakened structure invariably results. Often cracking was observed in the redeposited copper regions associated with the heat affected zones [1,31,34]. HAZ corrosion was considered to be potentially the more dangerous as corrosion could be continuous around the periphery of the weld, whereas crevice corrosion on the body of the casting tended to be small and isolated, and not penetrate to any appreciable depth [1,4]. It has been suggested [37] that corrosion beneath the barnacles may be caused by sulphate-reducing bacteria *Spirovibrio desulfuricans*; however, sulphides have not been detected, which points to differential aeration as the more likely mechanism. Corrosion was reported to cease immediately the crevice conditions were removed. Work using chemical agents to prevent marine biofouling has been undertaken. It has been claimed [35] that anti-biofouling measures need only be taken when the ship is in harbour or under slow running conditions in coastal waters. Both dousing with chlorine and Cu^{2+} ions have been found to be effective in preventing marine surface growths [35].

The corrosion products formed under crevice conditions are often powdery and adhere loosely, and so can be removed simply by agitating in water [39].

The selective phase corrosion of the β phase within the weld deposit has been overcome by using matching weld deposits followed by suitable post weld heat-treatment [1,4].

9. EFFECT OF HEAT-TREATMENT ON CORROSION RESISTANCE

Heat-treating samples at either 675°C for 6 hours or 830°C for 2 hours significantly improves the HAZ corrosion resistance in a sea water environment [1,4,36]. After the low temperature treatment very little selective phase attack is reported, although the microstructure is similar to that in the as-cast condition where significant corrosion is reported [4]. However, some coarsening and increased κ V precipitation within the α grains along with conversion of any retained β to $\alpha + \kappa$ would have been expected in accordance with transformations reported earlier in section 5.1.

The higher temperature heat-treatments tend to break up the lamellar phase making it less continuous, [4,36] thus restricting any selective corrosion penetration to the surface layers. This advantage can be offset however, by the retention of the high temperature β phase [1,4,36]. Significant HAZ corrosion has been reported where this phase occurred in the microstructure as a continuous grain boundary network [4].

Under crevice conditions away from the HAZ areas, similar corrosion rates are experienced for the as-cast material and both heat-treatment temperatures [4].

It is claimed that the ideal structure from a corrosion resistance view point is a β -free structure, with as little κ III as possible in the isolated condition [33,34]. However, such structures can only be achieved with complex heat-treatments which in some instances are not practical. Furthermore, such structures may conflict with the strength requirements of naval specifications [29].

10. SUMMARY

Development programmes in both the US and UK directed at improving NAB casting alloys have overcome many of the early corrosion problems associated with submarine valves by altering welding procedures, introducing post weld heat-treatments, initiating tighter alloy specifications, and introducing improved foundry techniques. Current work indicates that there is no microstructural advantage in using the high temperature ($815 \pm 15^\circ\text{C}$) heat-treatment to improve corrosion resistance. Furthermore, there is a real risk that β may be formed in the thinner sections of castings or weld deposit areas where cooling rates are higher, causing a lowering of corrosion resistance. The lower tempering temperature of $675 \pm 15^\circ\text{C}$ appears to achieve all the desired microstructural features consistent with improved corrosion resistance without the risk of β formation. However, the finer precipitation within the α grains at the lower tempering temperatures could lead to difficulties in obtaining elongation and Charpy impact toughness values required by the DGS 348 specification. This can be overcome without any known detriment to the microstructure by heating at a slightly higher temperature of 710°C for a similar time or holding for longer periods (16 hours) at the conventional temperature [27].

There still appears to be no clear understanding as to how post weld heat-treatment achieves improved HAZ corrosion resistance. Culpan and Rose [4] consider that the changing electropotential of the α grains as a result of κ V precipitation during heat-treatment may be a factor in influencing the improved HAZ corrosion performance. Although it has been claimed [34] that there was no evidence to suggest that residual stresses were a major factor in influencing HAZ corrosion, Culpan and Rose [4] consider that it may be a factor. The fact that cracking in the copper redeposited region of the HAZ has been reported by a number of workers suggests that tensile stresses were acting within the corroding zone. However, the role that such a stress might

play is far from clear. From available information it would also appear that closer control of material composition and improved foundry techniques have considerably improved the quality of castings [39]. It is likely, therefore, that one or more of a number of changes has contributed to the better overall corrosion performance of castings in service [2,39].

Crevice corrosion, where tight fitting flanges are present or biofouling occurs, is still a problem in operational systems. Recent reports indicate that corrosion in castings which have been heat treated and subjected to tighter casting controls is less severe with penetration being confined to the surface grains [1,2,41]. Observations at MRL and elsewhere [4] have tended to confirm this viewpoint. As regards heat-treatment, no difference in crevice corrosion performance has been observed between the 800 and 675°C treatments. Furthermore the as-cast material can perform equally well [4]. However, in the latter case, corrosion performance may be influenced by poor foundry practice, particularly inappropriate cooling rates, which could lead to some β being retained in the microstructure. Again, there still does not appear to be any real understanding as to why certain areas of castings undergo pitting or crevice attack while other areas, apparently similar, remain immune.

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TABLE I
COMPOSITIONAL RANGES FOR NAB DGS-8520

Element	Not Less Than	Not more than
	Per Cent	
Aluminium	8.5	10.0
Iron	3.5	5.5
Nickel	4.5	6.5
Manganese	-	1.5
Zinc	-	0.50
Lead	-	0.03
Copper	The remainder	
Other Impurities		
Tin	-	0.10
Silicon	-	0.25
Magnesium	-	0.05
Total - including) 0.03% Max. Lead)	-	0.03

TABLE II
MECHANICAL PROPERTY REQUIREMENTS FOR NAB DGS-8520

Tensile Strength		0.1% Permanent Set Stress		Elongation	Izod	
N/mm ²	tonf/in ²	N/mm ²	tonf/in ²	Per cent	ft.lbs	Joules
Min		Min		Min	Min	Min
618	40	248	16	15	15	20

TABLE III

COMPOSITIONAL RANGES FOR NAB DGS-348

Element	Not less than	Not more than
	Per Cent	
Aluminium	8.8	9.5
Iron*	4.0	5.0
Nickel*	4.5	5.5
Manganese	0.15	1.3
Copper	The remainder	
Other Impurities		
Zinc	-	0.2
Lead	-	0.02
Tin	-	0.10
Silicon	-	0.10
Magnesium	-	0.05
Total Impurities	-	0.30

* Nickel Must Exceed Iron

TABLE IV

MECHANICAL PROPERTY REQUIREMENTS FOR N B DGS-348

Tensile Strength		0.2% Proof Stress		Elongation on 5.65 $\sqrt{S_0}$ Gauge Length
N/mm^2	tonf/in ²	N/mm^2	tonf/in ²	Per Cent
Min		Min		Min
587	38	230	15	15

TABLE V

VARIATION OF TRANSFORMATION TEMPERATURE WITH COOLING RATE

AFTER CULPAN ET AL [10]

Phase transformation	Equilibrium transformation temperature (°C)	"25 mm casting" transformation temperature (°C)
$\beta \rightarrow \alpha + \beta$	1010	925
$\beta \rightarrow \alpha + \kappa\text{I}$	900-920	820-830
$\beta \rightarrow \alpha + \kappa\text{II} + \kappa\text{III}$	840-870	775-750
$\alpha \rightarrow \alpha + \kappa\text{IV}$		700-675

TABLE VI
CHEMICAL ANALYSIS (WT%) FROM SEVERAL AUTHORS OF PHASES PRESENT IN CAST NICKEL ALUMINIUM BRONZE

Phase		SEM/bulk						STEM/Thin Foil					
Ref No.	4	Al	Si	Mn	Fe	Ni	Cu	Al	Si	Mn	Fe	Ni	Cu
α		8.3 \pm 1.7	-	1.4 \pm 0.1	2.7 \pm 2	2.5 \pm 1.4	85.4 \pm 4	8 \pm 2	-	0.8 \pm 0.3	2.4 \pm 1	3 \pm 2	86 \pm 4
β		8.7	-	1.0	1.6	3.5	85.2	-	-	-	-	-	-
κ I		13 \pm 5	-	2 \pm 0.4	55 \pm 7	15 \pm 3	15 \pm 5	-	-	-	-	-	-
κ II		19 \pm 3	-	2.2 \pm 0.6	32 \pm 3	27 \pm 4	21 \pm 5	18 \pm 4	-	1.6 \pm 0.3	34 \pm 5	24 \pm 5	23 \pm 4
κ III		18 \pm 6	-	2 \pm 0.3	22 \pm 0.7	32 \pm 2	26 \pm 4	22 \pm 4	-	1.6 \pm 0.4	22 \pm 5	28 \pm 5	26 \pm 4
κ IV		20 \pm 3	-	1.5 \pm 0.3	62 \pm 4	4 \pm 1	13 \pm 1	9 \pm 4	-	1.6 \pm 0.4	60 \pm 8	6 \pm 4	23 \pm 6
κ V		26	-	1.1	26	21	26	-	-	-	-	-	-
Spheroidised κ		19	-	1.6	35	24	21	-	-	-	-	-	-
Ref No.	12	SEM						TEM/Thin Foil (EMMA)					
κ II		14.7 \pm 0.4	3.3 \pm 0.3	2.3 \pm 0.6	40.0 \pm 8.5	8.9 \pm 1.4	31.9 \pm 9.1	-	-	-	-	-	-
κ III		-	-	-	-	-	-	24	0.8	1.9	15.00	30.5	27.7
κ IV		-	-	-	-	-	-	14.1	2.6	2.0	57.00	8.2	15.6
Globular κ		0.3 \pm 0.1	0.4 \pm 0.1	4.3 \pm 0.5	90.6 \pm 1.2	1.6 \pm 0.1	2.8 \pm 0.8	-	-	-	-	-	-

TABLE VII
CHEMICAL ANALYSIS (WT%) FROM SEVERAL AUTHORS OF THE PHASES PRESENT IN CAST NICKEL ALUMINIUM BRONZE

Phase	STEM/Replica						(XEMMA)	TEM/Replica					
	Al	Si	Mn	Fe	Ni	Cu		Al	Si	Mn	Fe	Ni	Cu
Ref 4							Ref 12						
α	--	-	--	--	-	-	α	-	-	-	-	-	-
β	-	-	-	-	-	-	β	-	-	-	-	-	-
κI	-	-	-	-	-	-	κI	-	-	-	-	-	-
κII	19 \pm 5	-	1.3 \pm 0.1	34 \pm 5	30 \pm 3	15 \pm 5	κII	-	-	-	-	-	-
κIII	-	-	-	-	-	-	κIII	28.7 \pm 2.4	0.9 \pm 0.6	2.0 \pm 0.3	18.0 \pm 3.8	38.4 \pm 2.2	12.0 \pm 1.8
Cruciform κIV	14 \pm 2	-	1.1 \pm 0.4	63 \pm 6	14 \pm 4	8 \pm 3	Cruciform κIV	9.2 \pm 0.7	3.1 \pm 0.6	3.1 \pm 0.6	77.6 \pm 2.1	3.1 \pm 0.8	3.9 \pm 0.6
κV	27 \pm 4	-	1.5 \pm 0.3	27 \pm 4	35 \pm 3	10 \pm 2	Spheroidised κIV	6.2 \pm 0.8	3.1 \pm 0.7	2.9 \pm 0.9	81.0 \pm 2.1	2.7 \pm 0.6	4.1 \pm 1.6
Spheroidised κ	17 \pm 2	-	1.6 \pm 0.2	40 \pm 3	31 \pm 3	10 \pm 1	-	-	-	-	-	-	-
Ref 11	EPMA						Ref 38						
κI	10	-	-	69	8	13	α	6.5	-	-	3	7.5	87
κII	-	-	-	-	-	-	κI	14	-	-	64	6.5	9
κIII	18-20	-	-	26-43	23-34	13-20	($\kappa III + \alpha$)	9	-	-	3	3	82
κIV	-	-	-	-	-	-	($\kappa IV + \alpha$)	9	-	-	4	3	83

TABLE VIII
CHEMICAL ANALYSIS OF THE FINE PRECIPITATES WITHIN THE κ PHASE OF HEAT TREATED
NICKEL ALUMINIUM BRONZE AFTER CULPAN AND ROSE [10]

Phase	SEM/bulk					STEM/replica				
	Al	Mn	Fe	Ni	Cu	Al	Mn	Fe	Ni	Cu
κ IV globular phase (675°C for 2 h)						13 \pm 3	1 \pm 0.2	62 \pm 6	16 \pm 3	8 \pm 3
κ V lath phase (675°C for 2 h)						23 \pm 2	1 \pm 0.3	25 \pm 3	39 \pm 2	11 \pm 1
κ IV globular phase (675°C for 6 h)						14 \pm 2	1 \pm 0.5	63 \pm 6	14 \pm 5	8 \pm 5
κ V lath phase (675°C for 6 h)						27 \pm 4	1.5 \pm 0.3	27 \pm 4	35 \pm 3	10 \pm 2
κ V lath phase (675°C for 16 h)						20 \pm 3	1.3 \pm 0.3	34 \pm 3	35 \pm 2	10 \pm 1
κ V lath phase 740°C	26	1.1	26	21	26	21 \pm 2	1.8 \pm 0.5	33 \pm 3	35 \pm 2	9 \pm 2
κ V lath phase 790°C	23	1.2	33	21	22	18 \pm 2	1.6 \pm 0.3	40 \pm 2	30 \pm 1	10 \pm 1
κ V large lath phase 840°C	25	1.1	34	21	19	17 \pm 3	1.7 \pm 0.1	39 \pm 5	32 \pm 3	10 \pm 1
Spheroidized κ phase (840°C for 3 days)	19	1.6	35	24	21	17 \pm 2	1.6 \pm 0.2	40 \pm 3	31 \pm 3	10 \pm 1

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